

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-156169

(43)Date of publication of application : 15.06.1999

(51)Int.Cl.

B01D 67/00

B01D 61/10

B01D 69/12

(21)Application number : 09-337951

(71)Applicant : NITTO DENKO CORP

(22)Date of filing : 21.11.1997

(72)Inventor : HACHISUGA HISAO

IKEDA KENICHI

(54) REGENERATED ULTRAFILTRATION ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To reuse a reverse osmosis membrane element as an ultrafiltration membrane by treating a membrane surface of a composite reverse osmosis membrane element that has undergone membrane deterioration with at least one solution selected from the group of an aqueous solution of oxidizing agent, an aqueous solution of a reducing agent, and aqueous solution of an acid or alkali so as to remove an active layer on the membrane surface.

SOLUTION: When a composite reverse osmosis membrane element having a deteriorated performance due to membrane deterioration is treated, first the element is treated with an aqueous treatment solution so as to remove an active layer that has undergone performance deterioration. Treatment solutions are suitably, not limited, an aqueous solution of an oxidizing agent such as sodium hypochlorite, hydrogen peroxide, nitric acid, ozone or the like, and an aqueous solution of a reducing agent such as hydrazine, formic acid or the like, an aqueous solution of an acid such as hydrochloric acid, sulfuric acid or the like and an aqueous solution of an alkali such as sodium hydroxide, potassium hydroxide or the like. Next, the remaining solution on the element is removed and washed with water and drained off. The element thus obtained by these treatment is reused as a regenerated ultrafiltration membrane element.

LEGAL STATUS

[Date of request for examination]

13.11.2003

[Date of sending the examiner's decision of rejection]

BEST AVAILABLE COPY

[Kind of final disposal of application other

than the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application]

[Patent number] 3637751

[Date of registration] 21.01.2005

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against
examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ultrafiltration element reproduced from the compound reverse osmotic membrane element which carried out performance degradation by film degradation. This invention relates to the ultrafiltration element reproduced by carrying out decomposition removal of the barrier layer of the compound reverse osmotic membrane which carried out performance degradation in more detail. Reuse of the reverse osmotic membrane element which the engine performance fell by film degradation conventionally, and was discarded by regeneration of such a compound reverse osmotic membrane element is attained.

[0002]

[Description of the Prior Art] As current and a reverse osmotic membrane used widely industrially, there is asymmetric membrane of cellulose acetate and especially the lob type film (for example, U.S. Pat. No. 3,133,132, U.S. Pat. No. 3,133,137) is known widely. Moreover, the compound reverse osmotic membrane which comes to form the activity thin film which has selection separability substantially on a microporous supporting lamella as a reverse osmotic membrane in which structure differs from this is also known.

[0003] The things (for example, JP,55-147106,A, JP,62-121603,A, JP,63-218208,A, JP,2-187135,A, etc.) which formed the polyamide thin film specifically obtained according to the interfacial polymerization of polyfunctional aromatic amine and polyfunctional aromatic series acid halide on the supporting lamella as such a compound reverse osmotic membrane, or the thing in which the thin film which consists of a polyamide obtained according to the interfacial polymerization of polyfunctional aromatic amine and polyfunctional alicyclic acid halide was formed on the supporting lamella is known (for example, JP,61-42308,A etc.).

[0004] Usually, these reverse osmotic membranes are element-ized by gestalten, such as the shape of a spiral, and are used for various applications. If film contamination produces these reverse osmotic membrane element by use, since it is decontamination, washing will be performed. however, the repeat of such [a reverse osmotic membrane] washing etc. -- gradually -- deteriorating (increment in inhibition performance degradation or a water permeate flow (or fall)) -- just -- being alike -- the engine performance of the range of the original value of standard is no longer obtained, and it exchanges for a new element and comes to be discarded. Although adding various water soluble polymer solutions as an inhibition engine-performance restorative during operation is also performed to the inhibition performance degradation of a reverse osmotic membrane, it cannot be said to be the fundamental playback approach.

[0005] In recent years, importance is attached to the measure to environmental preservation, and the playback is strongly called for from a viewpoint of industrial waste reduction also about the used reverse osmotic membrane element.

[0006]

[Problem(s) to be Solved by the Invention] Membraneous ability falls and the purpose of this invention is conventionally to offer the approach of reproducing the reverse osmosis element canceled as use impossible, and using.

[0007]

[Means for Solving the Problem] As a result of examining many things about the aforementioned

technical problem, by removing the barrier layer of a reverse osmotic membrane, this invention persons acquire the knowledge that it is usable as ultrafiltration membrane, and came to complete this invention.

[0008] This invention processes the film front face of the compound reverse osmotic membrane element which carried out film degradation with at least one sort of solutions chosen from the oxidizer water solution, the reducing-agent water solution and the acid, or the alkali water solution, and offers the ultrafiltration element which might be removed in the barrier layer on the front face of the film.

[0009]

[A detailed explanation of invention] According to the playback approach of this invention, reverse osmotic membranes, such as various polyamide systems and a poly urea system, and a compound reverse osmotic membrane, especially the reverse osmotic membrane produced by interfacial polymerization are reproducible as ultrafiltration membrane.

[0010] The reverse osmotic membrane used for playback may be conventionally obtained by the well-known approach. After applying at least to one side of a porous polysulfone supporting lamella the monomer which has reactant amino groups, such as a meta-phenylenediamine, a piperazine, and polyethyleneimine, and/or the water solution of a polymer as such a reverse osmotic membrane, for example, it is making the hexane solvent of polyfunctional acid chloride, such as trimesic acid chloride, etc. contact, and the compound reverse osmotic membrane in which the coat which is made to perform an interfacial polymerization on a porous polysulfone supporting lamella, and has the demineralization engine performance was made to form is mentioned.

[0011] In order to process the aforementioned compound reverse osmotic membrane element which carried out performance degradation, first, an element is processed with aquosity processing liquid and the barrier layer which carried out performance degradation is removed. As processing liquid from which a barrier layer is removed here, although alkali water solutions, such as acid water-solution; sodium hydroxides, such as reducing-agent water-solution; hydrochloric acids, such as oxidizing agent water-solution; hydrazines, such as a sodium hypochlorite, a hydrogen peroxide, a nitric acid, and ozone, a formic acid, and an aldehyde, and a sulfuric acid, and a potassium hydroxide, etc. are used suitably, it is not limited to these. Moreover, these may use two or more sorts together.

[0012] The concentration of these processing liquid is 0.1 - 30 % of the weight preferably 0.01 to 50% of the weight. Although especially an approach is not limited, it is desirable to introduce processing liquid from the supply side of a processing undiluted solution, and to perform processing of 0.5 - 24 hours at the processing temperature of 10-60 degrees C.

[0013] After using processing liquid to a reverse osmotic membrane, the processing liquid which remains on a membrane element is fully removed, and a rinse ridge is performed further. It is not limited especially although it is efficient to introduce dry air into a ridge from the undiluted solution supply side of an element. In addition, it is more desirable not to perform desiccation completely, in order to control the permeable fall of a playback element.

[0014] The element obtained by such processing has engine performance sufficient as a playback ultrafiltration membrane element, for example, the inhibition engine performance of a polyethylene glycol (molecular weight 20,000) shows 10% or more of engine performance.

[0015]

[Example] This invention is not limited by these examples, although an example is given next and this invention is explained.

[0016] ES10-D2 element (: by NITTO DENKO CORP. -- the inhibition engine performance of NaCl500ppm -- the water permeate flow of 98% and 7.5 kgf/cm² -- 2.5m³/d) in which the [example 1] engine performance deteriorated was processed. The sodium-hypochlorite solution (10,000 ppm) was introduced, processing of 24 hours was performed, and the barrier layer on the front face of a reverse osmotic membrane was removed from the undiluted solution supply side of this reverse osmotic membrane element. Dry air was sprayed on the film surface and the superfluous moisture of a film surface was removed from the undiluted solution supply side after rinsing this element.

[0017] Thus, the processed membrane element was evaluated as an ultrafiltration membrane element. That is, when pressure 5 kgf/cm² estimated using the polyethylene glycol (molecular

weight 20,000), it is 85% of rejection, and water permeate flow 140 L/hr, and it was checked that a playback element can be used as an ultrafiltration membrane element.

[0018]

[Effect of the Invention] According to this invention, membraneous ability falls, and it can reproduce and use conventionally, being able to use as ultrafiltration membrane the reverse osmosis element canceled as use impossible.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-156169

(43) 公開日 平成11年(1999) 6月15日

(51) Int.Cl.⁶

識別記号

F I

B 0 1 D 67/00
61/10
69/12

B 0 1 D 67/00
61/10
69/12

審査請求 未請求 請求項の数 1 F D (全 3 頁)

(21) 出願番号 特願平9-337951

(22) 出願日 平成9年(1997)11月21日

(71) 出願人 000003964

日東電工株式会社
大阪府茨木市下穂積1丁目1番2号

(72) 発明者 蜂須賀 久雄

大阪府茨木市下穂積1丁目1番2号 日東
電工株式会社内

(72) 発明者 池田 健一

大阪府茨木市下穂積1丁目1番2号 日東
電工株式会社内

(74) 代理人 弁理士 森岡 博

(54) 【発明の名称】 再生限外濾過エレメント

(57) 【要約】

【課題】 膜性能が低下し使用不能として破棄されている逆浸透エレメントを再生、利用する。

【解決手段】 この発明は、膜劣化した複合逆浸透膜エレメントの膜表面を、酸化剤水溶液、還元剤水溶液、酸又はアルカリ水溶液などを含有する溶液により処理して、膜表面の活性層を除去し得られた限外濾過エレメントを提供する。

【特許請求の範囲】

【請求項1】 膜劣化した複合逆浸透膜エレメントの膜表面を、酸化剤水溶液、還元剤水溶液及び、酸又はアルカリ水溶液から選ばれた少なくとも1種の溶液により処理して、膜表面の活性層を除去し得られた限外濾過エレメント。

【発明の詳細な説明】

【0001】

【発明の分野】本発明は、膜劣化によって性能の低下した複合逆浸透膜エレメントから再生された限外濾過エレメントに関する。本発明はさらに詳しくは、性能劣化した複合逆浸透膜の活性層を分解除去して再生された限外濾過エレメントに関する。このような複合逆浸透膜エレメントの再生処理により、従来、膜劣化により性能が低下し廃棄されていた逆浸透膜エレメントの再利用が可能になる。

【0002】

【従来の技術】現在、工業的に広く用いられている逆浸透膜としては、酢酸セルロースの非対称膜があり、特にロブ型膜(例えば、米国特許第3,133,132号、米国特許第3,133,137号)が広く知られている。また、これとは構造の異なる逆浸透膜として、実質的に選択分離性のある活性薄膜を微孔性支持膜上に形成してなる複合逆浸透膜も知られている。

【0003】このような複合逆浸透膜として、具体的には多官能芳香族アミンと多官能芳香族酸ハロゲン化物との界面重合によって得られるポリアミド薄膜を支持膜上に形成したもの(例えば、特開昭55-147106号、特開昭62-121603号、特開昭63-218208号、特開平2-187135号等)、あるいは多官能芳香族アミンと多官能脂環式酸ハロゲン化物との界面重合によって得られたポリアミドからなる薄膜を支持膜上に形成したものが知られている(例えば、特開昭61-42308号等)。

【0004】通常、これらの逆浸透膜はスパイラル状等の形態にエレメント化され、各種用途に使用されている。これら逆浸透膜エレメントは使用により膜汚染が生じると、汚染除去のため洗浄が行われる。しかしながら、逆浸透膜は、このような洗浄の繰り返し等により徐々に劣化し(阻止性能の低下や透過水量の増加(又は低下))、ついには当初の規格値の範囲の性能が得られなくなり、新規エレメントと交換して廃棄されるに至る。逆浸透膜の阻止性能の低下に対しては、運転中に阻止性能回復剤として各種水溶性高分子溶液を添加することも行われているが根本的な再生方法とは言えない。

【0005】近年、環境保全に対する取り組みが重要視され、使用済の逆浸透膜エレメントについても産業廃棄物低減の観点からその再生が強く求められている。

【0006】

【発明が解決しようとする課題】本発明の目的は、膜性能が低下し従来は使用不能として破棄されていた逆浸透

エレメントを再生、利用する方法を提供することにある。

【0007】

【課題を解決するための手段】本発明者らは、前記の課題について種々検討を行った結果、逆浸透膜の活性層を除去することにより限外濾過膜として使用可能であるとの知見を得て本発明を完成するに至った。

【0008】本発明は、膜劣化した複合逆浸透膜エレメントの膜表面を、酸化剤水溶液、還元剤水溶液及び、酸又はアルカリ水溶液から選ばれた少なくとも1種の溶液により処理して、膜表面の活性層を除去し得られた限外濾過エレメントを提供するものである。

【0009】

【発明の詳述】本発明の再生方法によれば、種々のポリアミド系、ポリウレア系等の逆浸透膜及び複合逆浸透膜、特に界面重合法により製膜された逆浸透膜を限外濾過膜として再生することができる。

【0010】再生に用いられる逆浸透膜は、従来公知の方法によって得られたものであってよい。このような逆浸透膜としては、例えば、メタフェニレンジアミン、ピペラジン、ポリエチレンジアミン等の反応性アミノ基を有するモノマー及び/又は、ポリマーの水溶液を多孔性ポリスルホン支持膜の少なくとも片面に塗布した後、トリメチン酸クロライド等の多官能酸クロライドのヘキサソル媒等と接触させることで、多孔性ポリスルホン支持膜上に界面重合を行なわせ脱塩性能を有する皮膜を形成させた複合逆浸透膜などが挙げられる。

【0011】性能の低下した前記の複合逆浸透膜エレメントを処理するには、まずエレメントを水性処理液にて処理し、性能の低下した活性層を除去する。ここで活性層を除去する処理液としては、次亜塩素酸ナトリウム、過酸化水素、硝酸、オゾンなどの酸化剤水溶液；ヒドラジン、ギ酸、アルデヒドなどの還元剤水溶液；塩酸、硫酸などの酸水溶液；水酸化ナトリウム、水酸化カリウムなどのアルカリ水溶液等が好適に用いられるが、これらに限定されない。また、これらは2種以上を併用してもよい。

【0012】これら処理液の濃度は0.01～50重量%、好ましくは0.1～30重量%である。処理法は特に限定されないが、処理液を処理原液の供給側から導入し、処理温度10～60℃にて、0.5～24時間の処理を行うのが好ましい。

【0013】逆浸透膜に対し処理液を用いた後、膜エレメント上に残存する処理液を充分に除去し、さらに水洗し水切りを行う。水切りには乾燥空気をエレメントの原液供給側から導入するのが効率的であるが特に限定されない。なお、再生エレメントの透水性の低下を抑制するため、乾燥は完全には行わない方が好ましい。

【0014】このような処理により得られたエレメントは、再生限外濾過膜エレメントとして充分な性能を有

し、例えばポリエチレングリコール(分子量20,000)の阻止性能が10%以上の性能を示す。

【0015】

【実施例】つぎに実施例を挙げて本発明を説明するが、本発明はこれら実施例により限定されるものではない。

【0016】[実施例1]性能の劣化したES10-D2エレメント(日東電工(株)製:NaCl500ppmの阻止性能が98%、 7.5 kgf/cm^2 の透過水量が $2.5\text{ m}^3/\text{d}$)を処理した。この逆浸透膜エレメントの原液供給側より次亜塩素酸ナトリウム溶液(10,000 ppm)を導入して24時間の処理を行い、逆浸透膜表面の活性層を除去した。このエレメントを水洗後、原液供給側よ

り乾燥空気を膜面に吹き付け、膜面の過剰な水分を除去した。

【0017】このように処理した膜エレメントを限外濾過膜エレメントとして評価した。すなわち、ポリエチレングリコール(分子量20,000)を用い、圧力 5 kgf/cm^2 にて、評価したところ、阻止率85%、透過水量 140 L/hr であり、再生エレメントは限外濾過膜エレメントとして使用できることが確認された。

【0018】

10 【発明の効果】本発明によれば、膜性能が低下し従来は使用不能として破棄されていた逆浸透エレメントを限外濾過膜として再生、利用することができる。

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.